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FINAL REPORT

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THE EFFECT OF GRAIN SIZE ON THERMAL DIFFUSION IN METALS

J.P. Stark
Materials Science Laboratory
Department of Mechanical Engineering
The University of Texas at Austin
Austin, Texas 78712

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ABSTRACT

This research was concerned with the experimental and theoretical evaluation of the segregation of substitutional solutes in metal alloys resulting from the application of a temperature gradient. Metallurgical structure, namely grain size, is known to be an important factor in solute redistribution. Measurements were made to evaluate the influence of this parameter. Namely, it has been shown that grain size controls the nonequilibrium concentration of vacancies which in turn influence solute fluxes.

Experimental measurements have been made of the diffusion coefficient of silver in aluminum to determine the concentration of vacancies that exist in a temperature gradient. Since the diffusivity is proportional to the vacancy concentrations, the diffusivity of silver in aluminum at the cold end of a thermal diffusion sample will reflect the nonequilibrium vacancy concentration if it is present. These measurements have rigorously demonstrated that vacancy concentrations in single crystals do not follow thermal equilibrium in a temperature gradient, whereas similar measurements with polycrystalline aluminum demonstrate such equilibrium. Theoretical work also established the matrix theory for diffusion in crystals.

RESEARCH RESULTS

From previous experimental work in this laboratory, a grain size dependence of the heat of transport has been indicated. Also from theoretical work by Stark, a concentration dependence has been suggested. A series of experiments was started to examine both of these factors in a set of aluminum alloys.

The system chosen was aluminum and silver. In atomic percent alloys were prepared to .1% Ag in Al and 2% Ag in Al. These alloys were prepared from the elements of 5-9's purity in an induction furnace under an atmosphere of 5-9's argon. After the original melt, the alloys were allowed to cool, were remelted and cast. In the .10% alloy single crystals were grown from the melt, and the as-cast alloy provided the polycrystalline specimens. Single grain specimens were obtained from the 2% alloys by cold work and a subsequent recrystallizing anneal. The polycrystalline samples were again provided by the cast alloy. In both instances the polycrystalline specimens contained grains of approximately 2 mm in diameter. The test specimens were sectioned on a spark cutter, spark planed and given an acid etch. The specimens were sectioned to 1 cm x .5 cm x .1 cm. These samples were then annealed in a temperature gradient of 450°C for periods up to 700 hours. The anneal was done under a hydrogen atmosphere.

Neutron activation analysis with subsequent sectioning

and counting are being used to determine the concentration profiles.

Results of these experiments are yield values of the heat of transport that do not show a strong dependence on grain size but do indicate a dependence on concentration. The measured heat of transport of Ag in aluminum for the .1% alloy is zero. The values obtained for the 2% alloy are

$$q = -2.27 \pm .15 \text{ kcal/mole}$$

for the single crystal data and

$$q = -1.09 \pm .17 \text{ kcal/mole}$$

for the polycrystalline data.

The experimental program also includes a direct determination of the concentration of vacancies in aluminum which exist in a temperature gradient. The concentration of vacancies has been theorized by Stark* to attain a steady state nonequilibrium distribution consistent with a minimum in the rate of entropy production. To measure this concentration we are determining the diffusion coefficient for silver in single crystalline aluminum from the cold end of a sample exposed to a temperature gradient. The concentration of vacancies, C_v, should follow the distribution

$$C_v = C_v^e \alpha_o e^{(1-\gamma)\Delta H_v/KT}$$

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*J.P. Stark, Scripta Met. 5, 727 (1971).

where C_v^e is the equilibrium concentration, α_o is a constant, and γ is a nonequilibrium factor that will be unity if equilibrium exists. Current and complete measurements have indicated that $\gamma \neq 1$ for single crystalline aluminum as was expected theoretically. We find $\gamma = 0.35$ in that system. For single crystalline silver, $\gamma = 0.89$ and for copper $\gamma = 1.0$.

Such a remarkable result shows that thermal equilibrium is violated as far as the concentration of vacancies is concerned. Thermal equilibrium is a standard assumption in all current theories of nonequilibrium thermodynamics; consequently, such a result is expected to have a significant influence upon scientific thought in this area of research.

To increase understanding of the basis for this observation, similar measurements were performed in polycrystalline aluminum. Such measurements gave evidence of the influence of grain size upon the phenomena. Our measurements indicate that thermal equilibrium is not violated in the instance of the polycrystalline aluminum samples. The measurements essentially show that $\gamma = 1$ in that situation. This demonstrates that grain size is an important factor, as was initially believed.*

As a consequence of this work, we have generally shown that the equilibrium concentration of vacancies is generally a valid concept to use when fine grained polycrystalline materials

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*J.H. Matlock and J.P. Stark, Acta Met. 19, 923 (1971).

are used. With single crystals, however, such a concept will lead to erroneous predictions when samples are exposed to temperature gradients.

In all applications where temperature gradients are found, the rates of metallurgical processes will be influenced by such overequilibrium concentration of vacancies. This is true because the diffusion coefficient of substitutional solutes is proportional to the vacancy concentration. Consequently, such processes as coarsening and deterioration of structure will occur at accelerated rates. Further, such changes in microstructure are followed with alterations in those mechanical properties that are dependent upon structure. Hence, strength and ductility will be heavily influenced. Finally, creep is an ever-present problem at high temperatures. Such high temperature service implies the presence of large temperature gradients. Consequently, creep rates should be directly influenced by these conditions and be expected to occur much more rapidly.

Additional research in this program was directed towards the understanding of diffusion processes under conditions which are more complicated than occur by a single vacancy mechanism. Namely, to even begin to understand theoretically the influence of, say, divacancies, it was necessary to develop a whole new theory of diffusion in terms of matrices. Thus, in conjunction with J.R. Manning of the National Bureau of Standards, the author developed the matrix theory of self-

diffusion and the response to diffusion when applied fields are present. Numerous applications of this theory have been developed by the author to enhance the understanding of concentration effects on diffusion and the influence of multiple vacancy mechanisms.

PUBLICATIONS

J.P. Stark, "The Influence of Solute Pairs on Solute Diffusion in a Substitutional fcc Alloy," J. Appl. Phys. 43, 4406 (1972).

R.A. McKee and J.P. Stark, "The Influence of Two Vacancy Interactions on Substitutional Solute Diffusion in an fcc Alloy," Phys. Rev. B7, 613 (1973).

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R.A. McKee and J.P. Stark, "Violation of Thermal Equilibrium in a Thermomigration Experiment," Phys. Rev. B11, 1374 (1975).

J.R. Manning and J.P. Stark, "Complete Path Matrix Equations for Tracer Diffusion Coefficient and Correlation Factors," Phys. Rev. B12, 2075 (1975).

R.A. McKee and J.P. Stark, "Interpretation of Thermomigration Results in Aluminum and Aluminum Alloys," Acta Met. 23, 1145 (1975).

S.S. Khan, J.P. Stark, and S.M. Shih, "Diffusion of Silver in Polycrystalline Aluminum in a Temperature Gradient," Phys. Rev. (in press).

S.M. Shih and J.P. Stark, "Diffusion of Ag^{110} into Single Crystalline Copper in a Temperature Gradient," J. Appl. Phys. (in press).

S.M. Shih and J.P. Stark, "Diffusion of Ag^{110} into Single Crystalline Silver in a Temperature Gradient," Phys. Rev. (in press).

THESIS AND DISSERTATIONS

Ph.D. Dissertations

"Thermomigration in Aluminum" by R.A. McKee

"Diffusion in a Temperature Gradient" by Shin-Min Shih

M.S. Thesis

"Diffusion of Silver in Polycrystalline Aluminum in a Temperature Gradient" by S. Khan

PERSONNEL

In addition to the principal investigator, Mr. R.A. McKee was employed on this contract as a Ph.D. candidate and research assistant in Materials Science. Mr. McKee finished his dissertation during the Fall of 1974.

Also, Mr. Shin-Min Shih was employed as a Ph.D. candidate and research assistant in Chemical Engineering. Mr. Shih finished his dissertation in the Spring of 1977.

Finally, Mr. Salman S. Khan was employed as an M.S. candidate in Mechanical Engineering and research assistant. Mr. Khan finished his work in the Fall of 1975.

COUPLING

Also, the principal investigator has been working upon some of the theoretical problems associated with this research with Dr. J.R. Manning of the National Bureau of Standards. This cooperation has already resulted in three publications on the matrix theory of diffusion in crystals.

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